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Synchrotron radiation excited total reflection X-ray fluorescence quantitative analysis of Si wafer by absolute fluorescence intensity calculation

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Abstract

One of the principal industry standard means of measuring surface and near surface wafer contamination is the total reflection X-ray fluorescence (TXRF). Quantification by theoretical calculation of the absolute fluorescence intensity is introduced instead of the use of standards in the TXRF experiment using synchrotron radiation. The surface densities of contaminants in and on Si wafers are determined by comparing calculated results with measured intensities. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The fabrication of today's most advanced integrated circuits involves various processing steps such as oxidation, etching, metallization and wet chemical cleaning. As strong correlations have been found between the presence of metal contaminants on the wafer surfaces and the process yields and performance of integrated circuits the cleanliness of wafer surfaces has long been a subject of interest to the semiconductor industry. In this regard, the semiconductor industry has forecasted a need to detect surface contamination of transition metals on the order of 10^7 atoms/cm^2 [1]. This need cannot be met at present and therefore improved analytical technology is required. One of the more accepted analytical techniques in this industry is the total reflection X-ray fluorescence(TXRF) [2–5]. In TXRF, X-rays impinge onto the surface of a planar sample at a glancing angle below the critical angle for total external reflection. A small fraction of the incoming X-ray intensity decays into the surface of the Si down to a shallow depth, typically about 30 Å. Therefore, TXRF has very high sensitivity for contaminants near the wafer surface. Quantification is usually done by the use of standards. However, it appears that quantification using standards with relatively high concentration of contaminant often fails

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to achieve good results for ultra trace contaminants [4].

Because one of the advantages of synchrotron radiation is the absolute calculability of all its properties; we can calculate the absolute fluorescence intensity from a contaminant atom by performing proper integrations according to the experimental conditions. When the depth distribution of contaminant is known, quantitative analysis using the calculated absolute fluorescence intensities is possible. However, the depth distribution is not known in general except in some ideal cases.

In this article, the absolute fluorescence intensities of contaminants near the wafer surface are calculated theoretically taking account of the depth distribution of the contaminants. The calculated absolute intensities are used in quantification by comparing them with the measured intensities.

2. Absolute fluorescence intensity calculation

In a typical configuration of TXRF experiments using incident X-rays of narrow energy bandwidth, the absolute K_α fluorescence intensity from element i atoms within $z \sim z + dz$ below the wafer surface can be written as [6,7],

$$dP_{i,K\alpha}^{in}(\phi_0, z)$$

$$= I_0(1 - R(\phi_0))\phi_0 \pi R_{eff}^2 \eta \frac{\Omega_{eff}}{4\pi} p_K \omega_K g_{K\alpha}$$

$$\times \exp[-\mu_f t_f] \frac{\tau_i \rho_i(z)}{Re[\phi_r]} \exp\left[-\frac{\mu_{Si}}{Re[\phi_r]} z\right] dz \tag{1}$$

where I_0 = the incident X-ray intensity; $R(\phi_0)$ = the reflectivity at incident glacing angle ϕ_0

$$R(\phi_0) = \left|\frac{\phi_0 - \phi_r}{\phi_0 + \phi_r}\right|^2,$$

πR_{eff}^2 = the area of the wafer seen by the sensor through the guard ring installed in front of the detector

$$\pi R_{eff}^2 = \pi \left[R_s \left(\frac{2Z_s}{Z_s - Z_g} - 1\right)\right]^2,$$

R_s = the radius of the Si(Li) sensor; Z_s = the height of the Si(Li) sensor from the wafer surface; Z_g = the height of the guard ring from the wafer surface; η = the detection efficiency; Ω_{eff} = the average solid angle of the sensor seen from the wafer area, πR_{eff}^2; p_K = the absorption jump factor of the series K; ω_K = the fluorescence yield of the series K; $g_{K\alpha}$ = the probability that the K_α line takes place in preference to other K lines; μ_f = the total attenuation coefficient of the filter installed between the wafer and the detector; t_f = the thickness of the filter; τ_i = the mass photoelectric absorption coefficient of element i; $\rho_i(z)$ = the density of element i; $Re[\phi_r]$ = the real component of the refraction angle, ϕ_r; μ_{Si} = the total attenuation coefficient of Si.

In Eq. (1), it is assumed that the average solid angle is small enough and the radii of the Si(Li) sensor and guard ring are the same. The self absorption of the Si wafer is also neglected. Because we can, in general, neglect the difference between the total attenuation coefficient and the photoelectric absorption coefficient of Si in the energy range of TXRF spectrum, we can easily calculate the fluorescence intensity, SiK, from a Si wafer having uniform density distribution as follows by integrating Eq. (1)

$$P_{Si,K}(\phi_0) = I_0(1 - R(\phi_0))\phi_0 \pi R_{eff}^2 \eta \frac{\Omega_{eff}}{4\pi} p_K \omega_K$$

$$\times \exp[-\mu_f t_f] \tag{2}$$

Similarly, the fluorescence intensity of contaminants on the wafer surface is given by [8]

$$dP_{i,K\alpha}^{on}(\phi_0, z)$$

$$= I_0 \tau_i \rho_i(z) \pi R_{eff}^2 \eta \frac{\Omega_{eff}}{4\pi} p_K \omega_K g_{K\alpha}$$

$$\times \exp[-\mu_f t_f] \left[1 + R(\phi_0) + 2\sqrt{R(\phi_0)}\right.$$

$$\left.\times \cos\left(\frac{4\pi \phi_0 z}{\lambda_0} - \psi\right)\right] dz. \tag{3}$$

λ_0 is the wavelength of incident X-ray and ψ is defined as $\cos^{-1}(2\phi_0/(\phi_C - 1))$ only in the region of total reflection. ϕ_C is the critical angle of total reflection.

To calculate Ω_{eff} we need to calculate the restricted area of the Si(Li) sensor seen through the guard ring from a emission point on the wafer. Referring to Fig. 1, where r is greater than the radius of the sensor R_s, the solid angle, $\Omega(r)$ is written as [9]

$$\Omega(r) = 2\int_0^{\Phi_1}\int_{\Theta_1}^{\Theta_2}\sin\theta\,d\theta\,d\phi, \qquad (4)$$

where

$$\Phi_1 = \sin^{-1}\left\{\frac{R_s}{r}\left(\frac{R_{\text{eff}}^2 - r^2}{R_{\text{eff}}^2 - R_s^2}\right)^{1/2}\right\},$$

$$\Theta_1 = \tan^{-1}\left\{\frac{r\cos\phi - \left(R_s^2 - r^2\sin^2\phi\right)^{1/2}}{Z_g}\right\},$$

$$\Theta_2 = \tan^{-1}\left\{\frac{r\cos\phi + \left(R_s^2 - r^2\sin^2\phi\right)^{1/2}}{Z_s}\right\}.$$

Where r is smaller than R_s, Eq. (4) is simplified to

$$\Omega(r) = 2\pi - 2Z_s\int_0^\pi\left[Z_s^2 + \left\{r\cos\phi\right.\right.$$
$$\left.\left. + \left(1 - r^2\sin^2\phi\right)^{1/2}\right\}^2\right]^{-1/2}d\phi. \qquad (5)$$

With $Z_s = 14$ mm, $Z_g = 2$ mm, and $R_s = 1.5$ mm, Ω_{eff} calculated from $\Omega(r)$ is 27.0 msr in the given conditions.
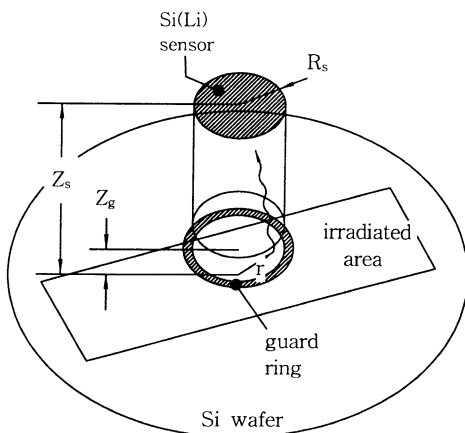

Fig. 1. Positions of the Si(Li) sensor and the guard ring over Si wafer.

3. Experimental

The source of the radiation used in this work was the beamline 10.32 on a bending magnet at the Advanced Light Source. The beam was focused horizontally by a spherical mirror in a 6:1 geometry and monochromated by a double multilayer monochromator coated with W/B4C of 50 layer pairs and a d-spacing of 25.6 Å. The obtained beam size in the full width of half-maximum was 6.0×0.06 mm in the vertical and horizontal planes, respectively. The primary reflected X-ray energy was 10.9 keV and the width in energy of the multilayer optic was roughly 200 eV. In addition to the primary reflection, the second harmonic was observed and its intensity was 0.02 of the first order X-ray flux. Other higher order harmonics may be suppressed by the mirror because the cutoff energy of the mirror is approximately 22 keV. The direct primary X-ray beam intensity was measured by using eight pieces of Mo foil that are 1-mm thick, the thickness was selected for reducing error due to higher order Bragg peaks, and the absorption factor of each foil was characterized by measuring intensity reduction of the primary X-ray flux. The measured flux of the direct X-ray beam transmitted by the double multilayer monochromator was 2×10^9 photons/s at 1.9 GeV electron energy and 30 mA current. The wafer was mounted with its surface normal horizontal so that the electric vector of the horizontally polarized X-ray beam was parallel to the surface normal. The chamber was evacuated up to $\sim 10^{-3}$ Torr during the experiments. The detector used for these experiments was a Si(Li) solid state detector with an intrinsic resolution of 140 eV at MnK$_\alpha$. The Si crystal of the detector was 1.8 mm in radius and 3 mm thick and a BN film of 12.5 μm thick was covered in front of the detector to shield it from visible light. A collimator 12 mm long was mounted in front of the detector to reduce the scattering intensity from the vertically polarized X-ray beam parallel to the wafer surface normal. As the collimator of 1.5-mm radius was extended from the guard ring to Si crystal, the effective dimension of the guard ring and the Si crystal could be well defined. Data was collected at 2 mm distance from the collimator end to the wafer surface.

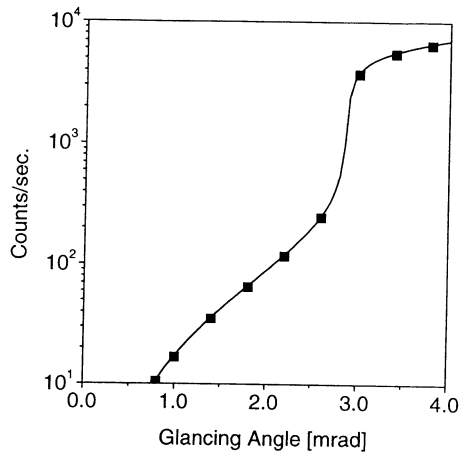Two kinds of Si wafers were supplied by the Hewlett Packard. One is a clean wafer prepared by

Fig. 2. SiK fluorescence intensity from the clean Si wafer as a function of the glancing angle. The solid line shows the calculated intensity from Eq. (2).

Fig. 4. CuK_α fluorescence intensity from the nominal clean Si wafer as a function of the glancing angle. The intensities calculated from the four depth distribution models are also shown.

industry standard cleaning processes. The other is a standard wafer artificially contaminated with 1×10^{12} atoms/cm^2 of Fe, Ni, and Zn.

4. Results and discussion

A series of X-ray spectrum was collected from both the contaminated and clean wafers. In order to compare the theoretical fluorescence intensity to the experimental result, X-ray spectra of the clean wafer
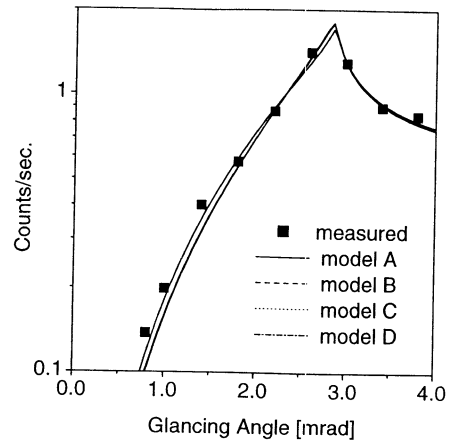
are collected at nine different glancing angles ϕ_0, which are 0.8, 1.0, 1.4, 1.8, 2.2, 2.6, 3.0, 3.4, and 3.8 mrad. First, the absolute fluorescence intensity calculation procedure is checked by comparing the result of Eq. (2) with measured SiK fluorescence intensities. As shown in Fig. 2, the calculated intensities agree well with the measured values at each of the various glancing angles. This shows that quantification by theoretical fluorescence intensity calculation is possible when we know the depth distribution of the analyte.

In the spectra from the nominal clean wafer, signals from Cu contaminant were present. To calculate the absolute fluorescence intensity $CuK\alpha$, four models of depth distribution, shown in Fig. 3, are suggested by investigating the glancing angle dependence of the measured intensities. The real depth distribution must be more complex in general, but
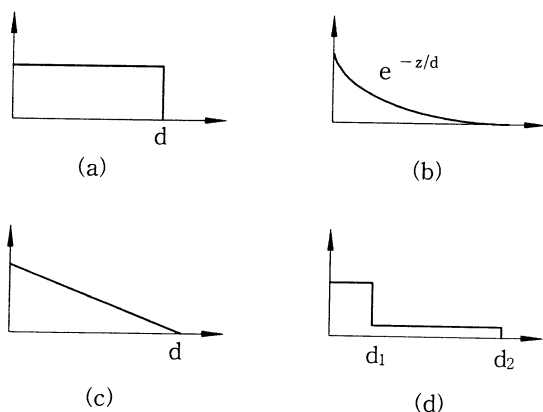

Fig. 3. Four depth distribution models of the Cu contamination in the nominal clean Si wafer. (a) model A, (b) model B, (c) model C, and (d) model D.

Table 1
Surface density of Cu contaminant in the nominal clean Si wafer calculated by Eq. (1) using various depth distribution models shown in Fig. 3

Model	d [Å]	ρ_s [atoms/cm^2]
A	43	6.43×10^{11}
B	25	6.47×10^{11}
C	67	6.44×10^{11}
D	0/288	6.59×10^{11}

the effect is discussed later. The value of d and the Cu surface density in each type of depth distribution are determined through data fitting using Eq. (1). The best fitting results are shown in Fig. 4 and the results are summarized in Table 1.

For model D, the best fit occurs for analyte just at the wafer surface combined with analyte with homogeneous density over 288 Å in depth. The surface density is calculated from the both of them. Table 1 shows that the surface density of Cu contaminant in this experiment could be determined independently of the real depth distribution. This means that quantification using theoretical fluorescence intensities can give good results for the surface density values if a depth distribution model properly fitting the angular dependence of measured fluorescence intensities is selected.

TXRF spectra for the Si wafer intentionally contaminated with 1×10^{12} atoms/cm^2 of Fe, Ni, and Zn are measured for three glancing angles of 1.4, 2.0, and 2.45 mrad chosen considering the overall measurement time and condition for the low minimum detection limit of typical TXRF experiment. The measurement at each glancing angle is repeated four times and the results are averaged. The spectra of each contaminants are fitted by Eq. (3) assuming homogeneous density distribution over a height d on
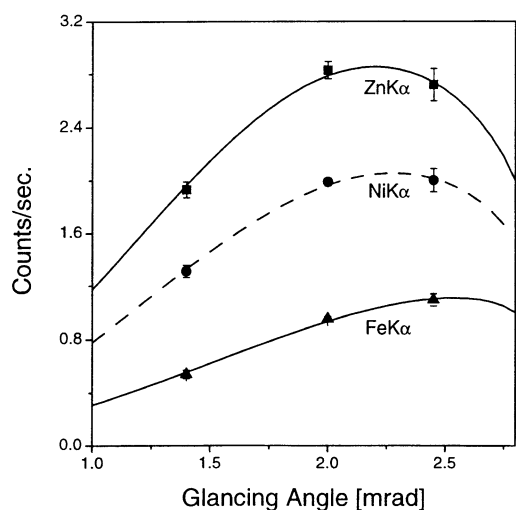
Table 2
Surface density of Fe, Ni, and Zn on the contaminated Si wafer calculated by Eq. (3) assuming homogenous distribution over a height d on the wafer surface

	d [Å]	ρ_s [atoms/cm^2]
Fe	69	8.54×10^{11}
Ni	103	1.08×10^{12}
Zn	113	1.02×10^{12}

the Si wafer surface. The best fitting results of three contaminants are shown in Fig. 5 and the results are summarized in Table 2. The surface density values are relatively close to the nominal values, although we have not checked the accuracy of the nominal values. In addition, the calculated surface densities are not much dependent on the depth distribution model used in fitting, as long as the fitting result is good enough.

In conclusion, we have calculated the absolute fluorescence intensity in SR-TXRF experimental condition. Quantification with the calculated absolute fluorescence intensity shows good results for the surface density of contaminants in and on Si wafer.

Acknowledgements

Fig. 5. FeK_α, NiK_α, and ZnK_α fluorescence intensity from the contaminated Si wafer for $\phi_0 = 1.4$, 2.0, and 2.45 mrad. The best fitting results using Eq. (3) are also shown.

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